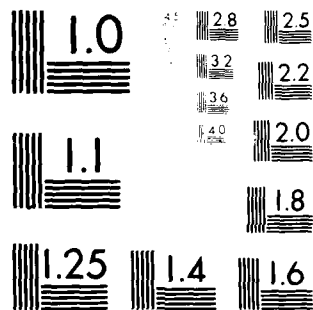AD-A098 277 ARMY ELECTRONICS RESEARCH AND DEVELOPMENT COMMAND FO--ETC F/G 7/4
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SIMPLIFIED ANALYSIS OF COMPLEX CONDUCTIVITY DATA

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MARK SALOMON

ELECTRONICS TECHNOLOGY & DEVICES LABORATORY

MARCH 1981

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)
A simplified method is presented for the analysis of conductivity data
for complex situations which involve ion pairing. The method was tested by
comparing results with more elaborate analyses using published data for a
number of salts in various solvents. The method is then used to analyze the
conductivity data for several salts in thionyl chloride. These latter
analyses are important for selecting electrolytes for lithium primary batteries.

CONTENTS

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SIMPLIFIED ANALYSIS OF COMPLEX CONDUCTIVITY DATA

INTRODUCTION

Conductivity measurements constitute some of the most accurate data which can be obtained in the laboratory. There is a long history of the theory and experimental techniques of conductivity data, and one of the most important features of this data is that it allows one to analyze the complex behavior of electrolyte solutions in solvents possessing a large range of dielectric constants. The development of the mathematical treatments of these data, particularly in analyzing for ion pair formation, has reached the point where sophisticated computational facilities are required. The purpose of this report is to present a method which simplifies the computational analyses, and at the same time retain the essential features of modern theory. A brief introduction to the analytical expressions for conductivity data for 1:1 electrolytes developed over the years will be given first.

The first expression developed by Onsager[1] which applies to very dilute solutions is:

$$\Lambda = \Lambda^{\infty} - (\Lambda^{\infty}\beta_1 + \beta_2) \, c^{\frac{1}{2}} = \Lambda^{\infty} - S \, c^{\frac{1}{2}} \tag{1}$$

Here Λ is the experimental molar conductivity for a completely dissociated salt at concentration c mol dm^{-3}, Λ^{∞} is the molar conductivity at infinite dilution, and β_1 and β_2 are constants which reflect upon ion-ion interactions. As early as 1883, Arrhenius proposed that the reason why Λ values for certain electrolytes were much smaller than expected was due to the association of ions. Arrhenius thus expressed the degree of ionization, α, of a salt in terms of conductivities as:

$$\alpha = \Lambda/\Lambda^{\infty} \tag{2a}$$

The equation holds at very high dilutions, and a more accurate expression for α is defined as the ratio of the experimental molar conductivity, Λ, to the molar conductivity Λ_f, which would be observed if the salt was completely ionized.

$$\alpha = \Lambda/\Lambda_f \tag{2b}$$

The chemical equation involving ion pairing of M^+ cations and X^- anions is given by

$$MX \rightleftharpoons M^+ + X^- \tag{3}$$

where MX is the undissociated ion pair. The thermodynamic dissociation

---

[1]L. Onsager, Z. Physik <u>27</u>, 388 (1926): <u>28</u>, 277 (1927).

constant for reaction (3) is given by:

$$K_D^o = [M^+][X^-]y_\pm^2/[MX]y_n \tag{4a}$$

where y_+ and y_n are, respectively, the mean molar activity coefficients for the ions and the neutral species MX. In terms of the degree of dissociation, Equation (4a) becomes:

$$K_D^o = \alpha^2 c\, y_\pm^2 /(1-\alpha)y_n \tag{4b}$$

and rearranging,

$$\alpha = 1 - \alpha^2 c\, y_\pm^2 /K_D^o\, y_n \tag{4c}$$

Taking Λ_f equal to that value given by the Onsager Equation (1), the equation for the experimental conductivity connected for ion pairing is obtained by combining Equations (1), (2b), and (4c):

$$\Lambda = \Lambda^\infty - S(\alpha c)^{\frac{1}{2}} - \Lambda\alpha c y_\pm^2/K_D^o\, y_n \tag{5}$$

A semiempirical form of Equation (5) has been developed by Fuoss and Kraus[2] and by Shedlovsky:[3]

$$\frac{1}{\Lambda F(z)} = \frac{1}{\Lambda^\infty} + \frac{\Lambda F(z)y_\pm^2 c}{K_D^o\,(\Lambda^\infty)^{3/2}} \tag{6}$$

In Equation (6), the activity coefficient y_n is assumed to equal unity, and the function F(z) is defined as follows:

$$F(z) = \left[(z/2)+ \left[1 + (z/2)^2\right]^{\frac{1}{2}}\right]^2 \tag{7}$$

and

$$z = S\,(\alpha c)^{\frac{1}{2}} /(\Lambda^\infty)^{3/2} \tag{8}$$

Equation (6), which suggests that Λ^∞ and $K_D^o\,(\Lambda^\infty)^{3/2}$ can be obtained from a plot of $1/\Lambda F(z)$ against $F(z)y_\pm^2\, c$, was used as the primary method of analysis for several decades. Its use is now being restricted since it still applies to very dilute solutions, and accurate Λ^∞ and K_D^o values are obtained only when K_D^o is in the range of 10^{-1} to 10^{-3} mol dm^{-3}. A major problem associated with the use of the Onsager Equation (1) is that it fails to account for higher order terms involving relaxation fields and electrophoretic velocity.

[2] R. M. Fuoss and C. A. Kraus, J. Am. Chem Soc. 55, 476 (1933).
[3] T. Shedlovsky, J. Franklin Inst. 225, 739 (1938).

One of the first attempts to produce a more accurate relation for expressing conductivity data was by Fuoss and Onsager:[4]

$$\Lambda = \Lambda^\infty - S\,c^{\frac{1}{2}} + E\,c\,\ln c + J\,c \tag{9}$$

where E is a constant dependent upon the nature of the solvent, and J is a constant dependent in part on the distance (R) of approach of the free ions. Combining Equations (2b), (4c), and (9) yields:

$$\Lambda = \Lambda^\infty - S\,(\alpha c)^{\frac{1}{2}} + E\,\alpha c\,\ln(\alpha c) + J\,\alpha c - \Lambda \alpha c y_\pm^2/K_D^O\,y_n \tag{10}$$

Later work[5] produced a more accurate expression which takes the form[6,7]

$$\Lambda = \Lambda^\infty - S\,c^{\frac{1}{2}} + E\,c\,\ln c + J_1 c - J_2\,c^{3/2} \tag{11}$$

Combining this equation with Equations (2b) and (4c) yields

$$\Lambda = \Lambda^\infty - S(\alpha c)^{\frac{1}{2}} + E\,\alpha c\,\ln(\alpha c) + J_1\,\alpha c - J_2(\alpha c)^{3/2} - \Lambda\,\alpha c y_\pm^2/K_D^O\,y_n \tag{12}$$

Both J_1 and J_2 are complex functions of the distance R, and complete analysis of Equation (12) requires the use of high speed computers. There is little doubt that both J_1 and J_2 terms are significant and essential for high accuracy. In solving Equation (12) for Λ^∞ and K_D^O, it is generally assumed that the extended Debye-Hückel relation (13) can be used for the mean molar activity coefficient,

$$\log y_\pm = -A\,(\alpha c)^{\frac{1}{2}}/\{\,1 + BR\,(\alpha c)^{\frac{1}{2}}\} \tag{13}$$

and that y_n is unity. In Equation (13), B is a constant and R is the distance of closest approach of the free ions. Since Justice[8] has presented convincing evidence that the distance R should be associated with the Bjerrum[9] critical distance q defined by

$$R = q = z^2 q^2/(\,2\,\epsilon kT), \tag{14}$$

much controversy [10,11] has been centered on the correct value for R. It is to be noted that if R is associated with q which has values about 10 times

[4] R. M. Fuoss and L. Onsager, J. Phys. Chem. 61, 668 (1957).
[5] R. M. Fuoss and K. L. Hsia, Proc. Nat. Acad. Sci. 57, 1550 (1967).
[6a] E. Pitts, Proc. Roy Soc. (London) A217, 43 (1953).
[6b] E. Pitts, B.F. Tabor, and J. Daly, Trans. Faraday Soc. 65, 849 (1969).
[7] R. Fernandez-Prini, "Physical Chemistry of Organic Solvent Systems," A. K. Covington and T. Dickinson, eds., Plenum Press, London, 1973.
[8] J.-C. Justice, J. Chim. Phys. 65, 353 (1968): Electrochim Acta 16, 701 (1971).
[9] N. Bjerrum, K. Danske Videnskab Selskab; Mat.-Fys.-Medd. 7, 9 (1926).
[10] R. Fernandez-Prini and J. E. Prue, Trans. Faraday Soc. 62, 1257 (1966).
[11] J.-C. Justice, R. Bury, and C. Treiner, J. Chim. Phys. 65, 1708 (1968).

greater than that required by Debye-Hückel theory, then by increasing $y_\pm$ (see Equation (13)),compensating changes will occur in the numerical values of J_1 and J_2. In order to simplify the analysis of Equation (12) and avoid the controversy involving the correct magnitude of R, a method has been developed which can be used with a hand-held calculator such as the TI-59 pocket calculator. The details of this method are discussed below and applications to numerous electrolytes and solvents are discussed which include analyses of conductivity data for systems of importance in lithium primary battery development.

METHOD

The Fuoss-Hsia Equation (12) is recast into an empirical form

$$\Lambda = \Lambda^\infty - S(\alpha c)^{\frac{1}{2}} + E \alpha c \ln(\alpha c) + J_1' \alpha c + J_2' (\alpha c)^{3/2} - \Lambda \alpha c y_\pm^2/K_D^O y_n \qquad (15)$$

where J_1' and J_2' are now empirical constants. The mean molar activity coefficient for the ions is also calculated empirically using the Davies equation

$$\log y_\pm = -A(\alpha c)^{\frac{1}{2}}/\left[1 + (\alpha c)^{\frac{1}{2}}\right] + 0.3 A\alpha c \qquad (16)$$

For the activity coefficient of the neutral ion pair, it is assumed that

$$\log y_n = 0.3 A\alpha c \qquad (17)$$

Equation (17) appears to hold well for aqueous solutions. Equation (15) can be rearranged in the form

$$Y = J_1' + J_2' (\alpha c)^{\frac{1}{2}} \qquad (18)$$

where

$$Y = \Lambda \{1 + y_\pm^2 \alpha c/(K_D^O y_n)\} / \alpha c - \{\Lambda^\infty - S(\alpha c)^{\frac{1}{2}} + E\alpha c\ell n(\alpha c)\}/\alpha c \qquad (19)$$

In evaluating Equation (18) by least squares, values of Λ^∞ and K_D^O are varied until the error,σ_Λ , in the observed conductivities is minimized. σ_Λ is defined by

$$\sigma_\Lambda = \{\Sigma (\Lambda_{obs} - \Lambda_{calc})^2/(N-3)\}^{\frac{1}{2}} \qquad (20)$$

where N is the number of data points. To perform the calculations, initial guesses at Λ^∞ and K_D^O are made, and α calculated by an iteration method using Equations (4b) and (16). The calculations are then repeated until σ_Λ is minimized by the appropriate Λ^∞ and K_D^O values. All calculations are begun by evaluating S, E, and the Debye-Hückel constants A and B:

$$A/mol^{-\frac{1}{2}} dm^{3/2} = 1.8246 \times 10^6/(\epsilon T)^{3/2} \qquad (21)$$

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$$B/cm \ mol^{-\frac{1}{2}}dm^{3/2} = 5.029 \times 10^7/(\varepsilon T)^{\frac{1}{2}} \tag{22}$$

For the Onsager constant $S = \Lambda^{\infty}\beta_1 + \beta_2$

$$\beta_1/mol^{-\frac{1}{2}}dm^{3/2} = 8.2046 \times 10^5/(\varepsilon T)^{3/2} \tag{23}$$

$$\beta_2/S \ cm^2 \ mol^{-3/2} \ dm^{3/2} = 82.487/\{\eta(\varepsilon T)^{\frac{1}{2}}\} \tag{24}$$

For the Fuoss-Onsager constant $E = \Lambda^{\infty}E_1 - E_2$,

$$E_1/mol^{-1}dm^3 = 2.94257 \times 10^{12}/(\varepsilon T)^3 \tag{25}$$

$$E_2/S \ cm^2 mol^{-1}dm^3 = 4.33244 \times 10^7/\{\eta \ (\varepsilon T)^2\} \tag{26}$$

Finally, the present method of treatment of conductivity data also permits a simple solution of Equation (10) by the least squares method; i.e.,

$$Y = J' - \Lambda y_{\pm}^2/K_D^O \ y_n \tag{27}$$

where

$$Y = \{\Lambda - \Lambda^{\infty} + S \ (\alpha c)^{\frac{1}{2}} - E \ \alpha c \ \ell n(\alpha c)\}/\alpha c \tag{28}$$

RESULTS

To test the accuracy of the present method for evaluating Λ^{∞} and K_D^O, the conductance data for various electrolytes in solvents having dielectric constants varying from $\varepsilon = 78.3$ D to $\varepsilon = 9.53$ D were analyzed and compared to previous results. The results of these analyses are given in Table 1 where all data refer to 25°C. The use of Equation (18) is seen to lead to equivalent values for Λ^{∞} and K_D^O when comparisons are made with the results obtained from the direct analyses of Equations (10) and (12). In several cases, the present method appears superior as indicated by much smaller σ_{Λ} values. In Table 2 results are given for the analyses of conductivity data for salts in thionyl chloride. These salts are all of interest for improvement of lithium primary batteries (Note: Pr_4N refers to the tetrapropylammonium ion $(C_3H_7)_4N^+$). The program written for the TI-59 calculator to solve Equation (15) is given in Appendix A.

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TABLE 1.* RESULTS OF ANALYSES OF CONDUCTIVITY DATA BY VARIOUS METHODS

Solvent $(\epsilon/D)(\eta/cP)$	Salt	Reference	N	$10^4 c_{max}$	Equation Number	J_1	J_2	Λ^∞ (σ)	K_D^0 (σ)	σ_Λ
water (78.30) (0.8903)	AgNO$_3$	12[a]	26	915				133.39	0.56	0.016
		13	?	?				133.43	1.157	0.028
			9	915	18	237.60	−279.77	133.43(0.04)	1.04(0.02)	0.030
			9	915	18b	235.09	−268.95	133.43(0.04)	1.06(0.02)	0.031
water	CH$_3$COOH	14[a]	10	100	c	.....	....	390.59	$1.753 \cdot 10^{-5}$	.....
			8	130	18	540.7	−52,872	390.70(0.16)	$1.751 \cdot 10^{-5}(1 \cdot 10^{-8})$	0.034
			8	130	27	−303.4	....	390.71(0.16)	$1.751 \cdot 10^{-5}(2 \cdot 10^{-8})$	0.029
acetonitrile (35.95) (0.3409)	Am$_4$NbAm$_4$	15[c]	7	29	10	1643.2	....	114.48	.....	0.04
		8[b]	7	29	12	2403	−7905	114.33(0.23)	0.42(0.16)	0.22
			7	29	18	2247.5	−8143.3	114.35(0.02)	0.70(0.11)	0.02
methanol (32.62) (0.5445)	Me$_4$NCl	16[a]	8	86	10	......	....	120.82	0.137	0.04
			8	85	18	2662.2	−6610.2	121.098(0.004)	$0.046(2 \cdot 10^{-5})$	0.003
n-propanol (20.33) (2.004)	Me$_4$NCl	17[a]	9	56	10	......	....	25.02	$2.19 \cdot 10^{-3}$	0.01
		8[b]	7	43	12	3126	−14846	25.29(0.07)	$1.70 \cdot 10^{-3}(5 \cdot 10^{-6})$	0.01
		18	7	43	10	......	....	25.05	$2.19 \cdot 10^{-3}$	0.01
		18	7	43	12	......	83.5	25.06	$2.13 \cdot 10^{-3}$	0.005
			7	43	18	1322.7	....	25.04(0.006)	$2.20 \cdot 10^{-3}(3 \cdot 10^{-6})$	0.004
			7	43	27	1328.4	....	25.04(0.006)	$2.20 \cdot 10^{-3}(2 \cdot 10^{-6})$	0.004
82 wt% p-dioxane in water (9.53) (1.671)	HCl	19[c]	21	41	6	......	....	57.5	$2.02 \cdot 10^{-3}$	.....
		8[b]	4	15	12	83300	−675000	57.93(0.08)	$2.03 \cdot 10^{-3}(2 \cdot 10^{-7})$	0.01
			4	15	18	52424	−279423	57.30(0.004)	$2.55 \cdot 10^{-3}(5 \cdot 10^{-8})$	0.002

*NOTES:

N is the number of data points and c_{max} is the highest concentration used in the calculations.

a - This is the reference to the original publications which contain the Λ and c data.

b - See Reference 8 for method.

c - See Reference 14 for method.

8 See page 3.

12 I. D. McKenzie and R. M. Fuoss, J. Phys. Chem. 73, 1501 (1960).

13 E. Hanna, A. D. Pethybridge, and J. E. Prue, Electrochim. Acta 16, 677 (1971).

14 D. A. MacInnes and T. Shedlovsky, J. Am. Chem. Soc. 54, 1429 (1932).

15 J. F. Coetzee and G. P. Cunningham, J. Am. Chem. Soc. 87, 2529 (1965).

16 R. L. Kay, C. Zawoyski, and D. F. Evans, J. Phys. Chem. 69, 4208 (1965).

17 D. F. Evans and P. Gardham, J. Phys. Chem. 72, 3281 (1968).

18 P. Beronius, Acta Chem. Scand. A29, 289 (1975).

19 B. B. Owen and G. W. Waters, J. Am. Chem. Soc. 60, 2371 (1938).

TABLE 2.[*] RESULTS OF ANALYSES BASED ON EQUATION (18) FOR SALTS IN $SOCl_2$

SALT	J_1	$-J_2$	$\Lambda^\infty (\sigma)$	$10^5 K_D^0 (\sigma)$	σ_Λ
$LiAlCl_4$	7.649×10^4	3.531×10^5	75.5 (1.7)	3.0 (0.1)	0.28
Pr_4NClO_4	1.015×10^5	2.142×10^5	106.2 (1.2)	6.0 (0.2)	0.72
Pr_4NCl	1.302×10^5	9.768×10^5	106.6 (1.3)	15.0 (0.6)	0.82
Pr_4NAlCl_4	8.411×10^4	8.149×10^4	97.0 (2.0)	10.0 (0.5)	0.88

*All data are for 25°C. Λ^∞ units are $S\ cm^2 mol^{-1}$, and K_D^0 units are $mol\ dm^{-3}$.

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APPENDIX A. -- TI-59 PROGRAM FOR SOLUTION OF EQUATION (15)

TITLE __Solution of equation 15_____ PAGE____OF_____ **TI Programmable**

PROGRAMMER ___M. Salomon_____ DATE _1980_____ **Program Record**

Partitioning (Op 17) |6.3.9. 39| Library Module ____N/A_____ Printer____.____ Cards____

USER INSTRUCTIONS

STEP	PROCEDURE	ENTER	PRESS		DISPLAY
1	Enter Debye-Hückel and Onsager constants	A		A	A
		β_1		R/S	β_1
		β_2		R/S	β_2
		E_1		R/S	E_1
		E_2		R/S	E_2
2	Enter Λ^∞	Λ^∞	2nd	A'	0
3	Enter K_D^o	K_D^o		B	0
4	Enter data for $i = 1,\ldots\ldots,n$	Λ_1		C	Λ_1
		c_1		R/S	c_1
		trial α		R/S	refined α_1
	If desired, read activity coefficients:			R/S	$y_\pm$
				R/S	y_n
5	Compute constants $J_1^!$ and $J_2^!$ and the			D	$J_1^!$
	correlation coefficient, r.			R/S	$J_2^!$
				R/S	r
6	Calculate standard deviations.			E	0
	(a)	Λ_1		R/S	Λ_1
	(b)	c_1		R/S	c_1
	(c)	refined α_1		R/S	-1
		.			.
		.			.
		.			.
		.			.
		α_n		R/S	$\sigma(\Lambda)$
				R/S	$\sigma(K_D^o)$
				R/S	$\sigma(\Lambda^\infty)$
7	Reset pointer to step 6(a)		2nd	E'	
8	Remove last set of Λ_1, c_1, α_1 from step 6.		2nd	B'	
9	After step 6 completed, to recalculate		2nd	D'	$\sigma(\Lambda)$
	the std devs, press 2nd D'			R/S	$\sigma(K_D^o)$
				R/S	$\sigma(\Lambda^\infty)$

8

000 76 LBL	059 42 STO	118 11 11	177 43 RCL
001 11 A	060 25 25	119 91 R/S	178 12 12
002 42 STO	061 71 SBR	120 43 RCL	179 34 FX
003 00 00	062 23 LNX	121 13 13	180 54)
004 91 R/S	063 71 SBR	122 91 R/S	181 95 =
005 42 STO	064 33 X²	123 43 RCL	182 22 INV
006 01 01	065 75 -	124 14 14	183 28 LOG
007 91 R/S	066 43 RCL	125 91 R/S	184 42 STO
008 42 STO	067 25 25	126 76 LBL	185 13 13
009 02 02	068 95 =	127 32 X:T	186 33 X²
010 91 R/S	069 50 IXI	128 01 1	187 65 ×
011 42 STO	070 22 INV	129 52 EE	188 43 RCL
012 03 03	071 77 GE	130 06 6	189 12 12
013 91 R/S	072 00 00	131 94 +/-	190 55 ÷
014 42 STO	073 86 86	132 32 X:T	191 43 RCL
015 04 04	074 43 RCL	133 92 RTN	192 14 14
016 91 R/S	075 11 11	134 76 LBL	193 95 =
017 76 LBL	076 66 PAU	135 25 CLR	194 42 STO
018 16 A'	077 65 ×	136 00 0	195 15 15
019 42 STO	078 43 RCL	137 42 STO	196 92 RTN
020 05 05	079 10 10	138 34 34	197 76 LBL
021 65 ×	080 95 =	139 42 STO	198 59 INT
022 43 RCL	081 42 STO	140 35 35	199 42 STO
023 01 01	082 12 12	141 42 STO	200 09 09
024 85 +	083 61 GTO	142 36 36	201 91 R/S
025 43 RCL	084 00 00	143 42 STO	202 42 STO
026 02 02	085 57 57	144 37 37	203 10 10
027 95 =	086 71 SBR	145 42 STO	204 91 R/S
028 42 STO	087 45 YX	146 38 38	205 42 STO
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035 75 -	094 43 RCL	153 00 00	212 12 12
036 43 RCL	095 15 15	154 65 ×	213 92 RTN
037 04 04	096 55 ÷	155 43 RCL	214 76 LBL
038 95 =	097 43 RCL	156 12 12	215 45 YX
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041 71 SBR	100 75 -	159 03 3	218 05 05
042 25 CLR	101 43 RCL	160 95 =	219 75 -
043 91 R/S	102 16 16	161 22 INV	220 43 RCL
044 76 LBL	103 95 =	162 28 LOG	221 06 06
045 12 B	104 55 ÷	163 42 STO	222 65 ×
046 42 STO	105 43 RCL	164 14 14	223 43 RCL
047 08 08	106 12 12	165 28 LOG	224 12 12
048 71 SBR	107 95 =	166 75 -	225 34 FX
049 25 CLR	108 42 STO	167 43 RCL	226 85 +
050 91 R/S	109 19 19	168 00 00	227 43 RCL
051 76 LBL	110 43 RCL	169 65 ×	228 12 12
052 13 C	111 12 12	170 43 RCL	229 65 ×
053 71 SBR	112 34 FX	171 12 12	230 23 LNX
054 59 INT	113 42 STO	172 34 FX	231 65 ×
055 71 SBR	114 20 20	173 55 ÷	232 43 RCL
056 32 X:T	115 71 SBR	174 53 (	233 07 07
057 43 RCL	116 44 SUM	175 01 1	234 95 =
058 11 11	117 43 RCL	176 85 +	235 42 STO

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236  16  16      295  95  =       354  42  STO     413  32  30
237  54  )       296  44  SUM     355  18  18      414  91  R/S
238  92  RTN     297  37  37      356  91  R/S     415  71  SBR
239  76  LBL     298  43  RCL     357  43  RCL     416  59  INT
240  33  X²      299  19  19      358  17  17      417  71  SBR
241  53  (       300  44  SUM     359  91  R/S     418  45  Y^x
242  43  RCL     301  38  38      360  43  RCL     419  71  SBR
243  08  08      302  33  X²      361  36  36      420  23  LNX
244  65  ×       303  44  SUM     362  55  -       421  43  RCL
245  43  RCL     304  39  39      363  43  RCL     422  16  16
246  14  14      305  92  RTN     364  34  34      423  85  -
247  55  -       306  76  LBL     365  75  -       424  43  RCL
248  43  RCL     307  14  D       366  53  (       425  18  18
249  13  13      308  43  RCL     367  43  RCL     426  65  ×
250  33  X²      309  34  34      368  35  35      427  43  RCL
251  95  =       310  65  ×       369  55  -       428  12  12
252  42  STO     311  43  RCL     370  43  RCL     429  85  +
253  21  21      312  36  36      371  34  34      430  43  RCL
254  33  X²      313  75  -       372  54  )       431  17  17
255  85  +       314  43  RCL     373  33  X²      432  65  ×
256  04  4       315  35  35      374  95  =       433  53  (
257  65  ×       316  33  X²      375  34  √x      434  43  RCL
258  43  RCL     317  95  =       376  42  STO     435  12  12
259  21  21      318  42  STO     377  23  23      436  45  Y^x
260  65  ×       319  22  22      378  43  RCL     437  03  3
261  43  RCL     320  35  1/x     379  39  39      438  54  )
262  10  10      321  65  ×       380  55  -       439  34  √x
263  95  =       322  53  (       381  43  RCL     440  95  =
264  34  √x      323  43  RCL     382  34  34      441  55  -
265  75  -       324  34  34      383  75  -       442  53  (
266  43  RCL     325  65  ×       384  53  (       443  01  1
267  21  21      326  43  RCL     385  43  RCL     444  85  +
268  95  =       327  37  37      386  38  38      445  43  RCL
269  55  -       328  75  -       387  55  -       446  15  15
270  02  2       329  43  RCL     388  43  RCL     447  55  ÷
271  55  -       330  38  38      389  34  34      448  43  RCL
272  43  RCL     331  65  ×       390  54  )       449  08  08
273  10  10      332  43  RCL     391  33  X²      450  54  )
274  95  =       333  35  35      392  95  =       451  95  =
275  42  STO     334  54  )       393  34  √x      452  75  -
276  11  11      335  95  =       394  35  1/x     453  43  RCL
277  54  )       336  42  STO     395  65  ×       454  09  09
278  92  RTN     337  17  17      396  43  RCL     455  95  =
279  76  LBL     338  43  RCL     397  17  17      456  33  X²
280  44  SUM     339  36  36      398  65  ×       457  42  STO
281  01  1       340  65  ×       399  43  RCL     458  27  27
282  44  SUM     341  43  RCL     400  23  23      459  44  SUM
283  34  34      342  38  38      401  95  =       460  30  30
284  43  RCL     343  75  -       402  91  R/S     461  43  RCL
285  20  20      344  43  RCL     403  76  LBL     462  09  09
286  44  SUM     345  35  35      404  15  E       463  65  ×
287  35  35      346  65  ×       405  00  0       464  43  RCL
288  33  X²      347  43  RCL     406  42  STO     465  15  15
289  44  SUM     348  37  37      407  29  29      466  55  -
290  36  36      349  95  =       408  42  STO     467  53  (
291  34  √x      350  55  -       409  30  30      468  43  RCL
292  65  ×       351  43  RCL     410  42  STO     469  16  16
293  43  RCL     352  22  22      411  31  31      470  85  +
294  19  19      353  95  =       412  42  STO     471  43  RCL
```

472	18	18	531	65	×	590	31	31
473	65	×	532	43	RCL	591	55	-
474	43	RCL	533	12	12	592	43	RCL
475	12	12	534	34	√x	593	33	33
476	85	+	535	54	)	594	95	=
477	43	RCL	536	85	+	595	34	√x
478	17	17	537	43	RCL	596	91	R/S
479	65	×	538	02	02	597	43	RCL
480	53	(	539	65	×	598	32	32
481	43	RCL	540	43	RCL	599	55	-
482	12	12	541	12	12	600	43	RCL
483	45	Y^x	542	34	√x	601	33	33
484	03	3	543	95	=	602	95	=
485	54	)	544	55	÷	603	34	√x
486	34	√x	545	53	(	604	91	R/S
487	75	-	546	01	1	605	76	LBL
488	43	RCL	547	75	-	606	17	B'
489	09	09	548	43	RCL	607	43	RCL
490	54	)	549	01	01	608	27	27
491	95	=	550	65	×	609	94	+/-
492	75	-	551	43	RCL	610	44	SUM
493	43	RCL	552	12	12	611	30	30
494	08	08	553	34	√x	612	43	RCL
495	95	=	554	54	)	613	28	28
496	33	X²	555	75	-	614	94	+/-
497	42	STO	556	43	RCL	615	44	SUM
498	28	28	557	05	05	616	31	31
499	44	SUM	558	95	=	617	01	1
500	31	31	559	33	X²	618	94	+/-
501	43	RCL	560	44	SUM	619	44	SUM
502	09	09	561	32	32	620	29	29
503	65	×	562	43	RCL	621	61	GTO
504	53	(	563	34	34	622	04	04
505	01	1	564	32	X:T	623	14	14
506	85	+	565	01	1	624	76	LBL
507	43	RCL	566	44	SUM	625	10	E'
508	15	15	567	29	29	626	61	GTO
509	55	÷	568	43	RCL	627	04	04
510	43	RCL	569	29	29	628	14	14
511	08	08	570	67	EQ	629	76	LBL
512	54	)	571	05	05	630	19	D'
513	75	-	572	77	??	631	61	GTO
514	43	RCL	573	94	+/-	632	05	05
515	12	12	574	61	GTO	633	01	01
516	65	×	575	04	04			
517	23	LNX	576	14	14			
518	65	×	577	75	-			
519	43	RCL	578	03	3			
520	07	07	579	95	=			
521	75	-	580	42	STO			
522	43	RCL	581	33	30			
523	12	12	582	35	1/x			
524	65	×	583	65	×			
525	53	(	584	43	RCL			
526	43	RCL	585	30	30			
527	18	18	586	95	=			
528	85	+	587	34	√x			
529	43	RCL	588	91	R/S			
530	17	17	589	43	RCL			